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ANALYSIS OF SORBENTS AND CATALYSTS
USED DURING A 90-DAY MANNED TEST

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For

Langley Research Center

NATIONAL AERONAUTICS and SPACE ADMINISTRATION

ANALYSIS OF SORBENTS AND

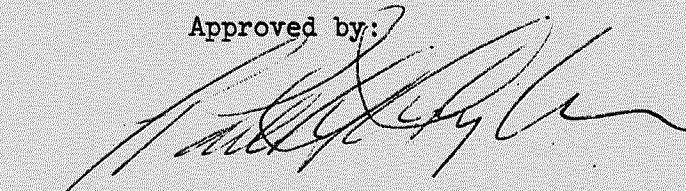CATALYSTS USED DURING A

90-DAY MANNED TEST

July 1971

By

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FOREWORD

The work described herein was conducted for the NASA Langley
Research Center under the direction of Mr. A. O. Pearson of
the Space Systems Division. The work was performed by the
Biotechnology and Power Department of the McDonnell Douglas
Astronautics Company, Huntington Beach, California, under NASA
Contract No. NAS1-8997.

This report was prepared by P. P. Mader, Ph.D., the principal
investigator for McDonnell Douglas, and A. S. Lucero.

ABSTRACT

Materials desorbed from three sorbent beds and from two catalysts used during
a 90-day manned test were identified and quantified. Since these sorbents,
in addition to their prime function, also showed the tendency to adsorb and
accumulate trace contaminants from the atmosphere, this capacity was investi-
gated and compared. The results indicated that the amounts of organic materials
adsorbed by molecular sieve were lower than those adsorbed by silica gel. The
largest quantities of organics were adsorbed by activated charcoal.

The number of identified organic compounds and their concentrations were far
below those identified and measured during the 60-day run. These data indicated
that the air inside the Space Station Simulator was of very high purity.

The action of Hopcalite and nickel catalysts may be gradually reduced or com-
pletely lost by interaction with halogenated organic compounds. These com-
pounds were formed by the thermal degradation of Freon 113 and were found to be
present in both catalysts after the 90-day test.

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Section 1

INTRODUCTION AND SUMMARY

During the recent 90-day manned test several different types of sorbents
and catalysts were used in the various subsystems of the life support system.
The adsorbents included: silica gel, molecular sieve and activated charcoal.
Catalysts that were used included nickel on Kieselgur in the Sabatier reactor
and Hopcalite for oxidation of trace contaminants in the atmosphere.

The various materials, in addition to their regular functions, showed the
ability to accumulate sizeable concentrations of organic and inorganic compounds
that were present in the atmosphere during closed manned tests. Reference 1
presents results of post-test analyses of sorbent beds after the 60-day test.
The study reported herein is intended to provide comparative data on the 90-day
manned test. Complete results of the 90-day test are reported in Reference 2
and summarized in Reference 3.

Accurate knowledge of the types and amounts of contaminants adsorbed by the
various sorbents and catalysts is important because (1) substitution of present
regenerative systems by more advanced techniques may affect the control of trace
contaminants within the cabin atmosphere and (2) the efficiency of certain
catalysts presently in use may be greatly reduced or completely destroyed by
interaction with contaminants identified in the atmosphere of the Space Station
Simulator (SSS).

The principal objectives of this program were to evaluate the sorbents' and
catalysts' capability to adsorb and remove contaminants, to determine the com-
position and quantities of adsorbed contaminants, and to determine the extent
to which the adsorbent bed or catalyst may have been altered by the chemical
interaction with the trace contaminants.

To accomplish the objectives of this program, the following tasks were performed: (1) two-gas chromatographs to be used for qualitative and quantitative determination of organic compounds were calibrated by determining elution times for two temperatures and two column packing materials; (2) a procedure was established to provide the optimum conditions for the desorption of organic compounds from the sorbents used during the 90-day run; (3) compounds released by the three sorbents were identified and quantitated; and (4) the nickel and Hopcalite catalysts used inside the SSS were analyzed and compared with unused material.

The results of this study may be summarized as follows:

Qualitative analyses of desorbates from silica gel, molecular sieve and activated charcoal beds led to the identification of 12-14 organic comtaminants. This compares to approximately 40 compounds identified after the 60-day run (Reference 1). The quantities of contaminants released by the 3 sorbents were also significantly lower. Both observations confirmed the high quality of the atmosphere inside the SSS.

Amounts of organic compounds desorbed from silica gel sorbent were considerably higher than from molecular sieve. These beds were desorbed every 45 minutes during approximately 20 days when the unit was in operation during the 90-day test. The highest amounts of organic compounds were driven off the activated charcoal bed. This sorbent had been in continuous use during the entire 90-day run. Neither silica gel nor molecular sieve sorbents showed the presence of ammonia, oxides of nitrogen or sulfur dioxide. Activated charcoal was found to desorb ammonia and oxides of nitrogen.

Hopcalite and nickel catalysts may be gradually deactivated or completely destroyed by interaction with halogenated compounds (Reference 4). These compounds may be formed by thermal degradation of Freon 113 which had been found in the SSS atmosphere. Their presence was detected in both catalyst materials which were used during the test period.

Section 2

SOURCES OF SAMPLES OF SORBENT BEDS AND CATALYSTS

2.1 Molecular Sieve and Silica Gel Sorbents

The molecular sieve and silica gel sorbents used in this project were obtained from the sorbent beds of the regenerable CO_2 concentrator shown in Figures 1 and 2. The concentrator included two molecular sieve beds for the removal of carbon dioxide. Since molecular sieve would preferentially adsorb any traces of atmospheric moisture thus reducing their CO_2 adsorption capacity, two silica gel beds were provided in the system to remove the moisture content of the circulated atmosphere. The beds were arranged so that one pair of sorbent beds adsorbed and accumulated water and carbon dioxide during a 45-minute cycle while the other pair were heated to $423^{\circ}K$ and the molecular sieve was evacuated to about 134 kN/m^2 (100 mm Hg) in order to release the previously loaded gases thereby regenerating the sorbent beds. The desorbed CO_2 was then transferred by a compressor to an accumulator for the processing in the Sabatier reactor.

The silica gel and molecular sieve samples evaluated in this study were taken after the concentrator was shutdown with the beds near the end of the adsorbing and desorbing operation portions of the cycle.

2.2 Activated Charcoal

The activated charcoal samples used in this project were taken from the charcoal bed that formed a part of the wick evaporator unit shown in Figures 3 and 4. The basic components of this unit were: six wick packages, blower, carbon filter, particulate filter and zero-g condenser/separator. During the 90-day run this unit was used as a backup for the Vacuum Distillation-Vapor Filtration (VD-VF) unit.
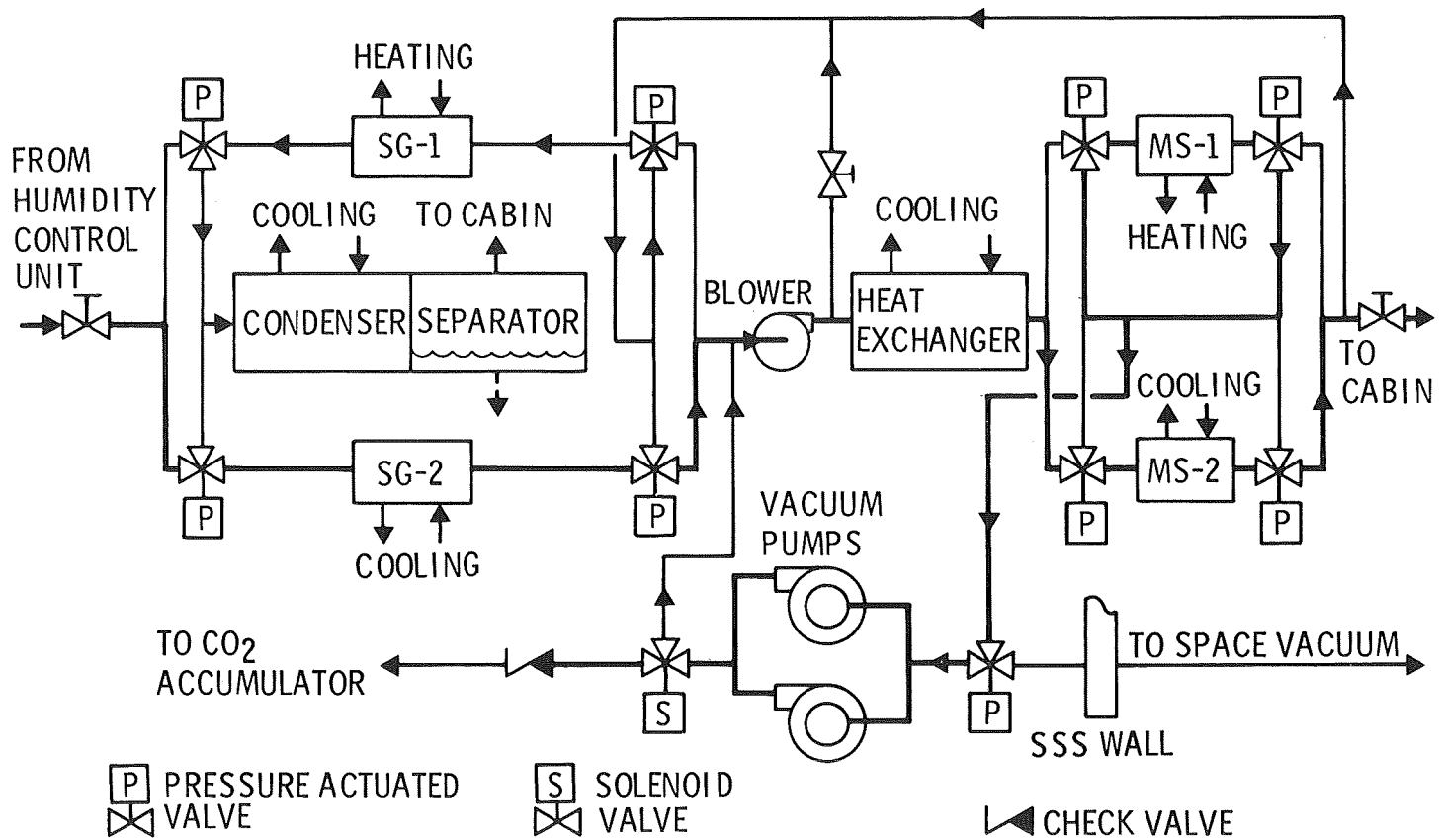
Figure 1. CO_2 Concentrator—Molecular Sieve Unit

MANUAL/AUTO SELECTOR

WATT METERS

RELAY ACCESS PANEL

STATUS LIGHTS AND MANUAL CONTROL SWITCHES

SILICA GEL ΔP GAGES

DISCHARGE PUMP GAGE

UNIT ΔP GAGES

MOLECULAR SIEVE ΔP GAGES

ISOLATION VALVES

COOLANOL ΔP GAGES
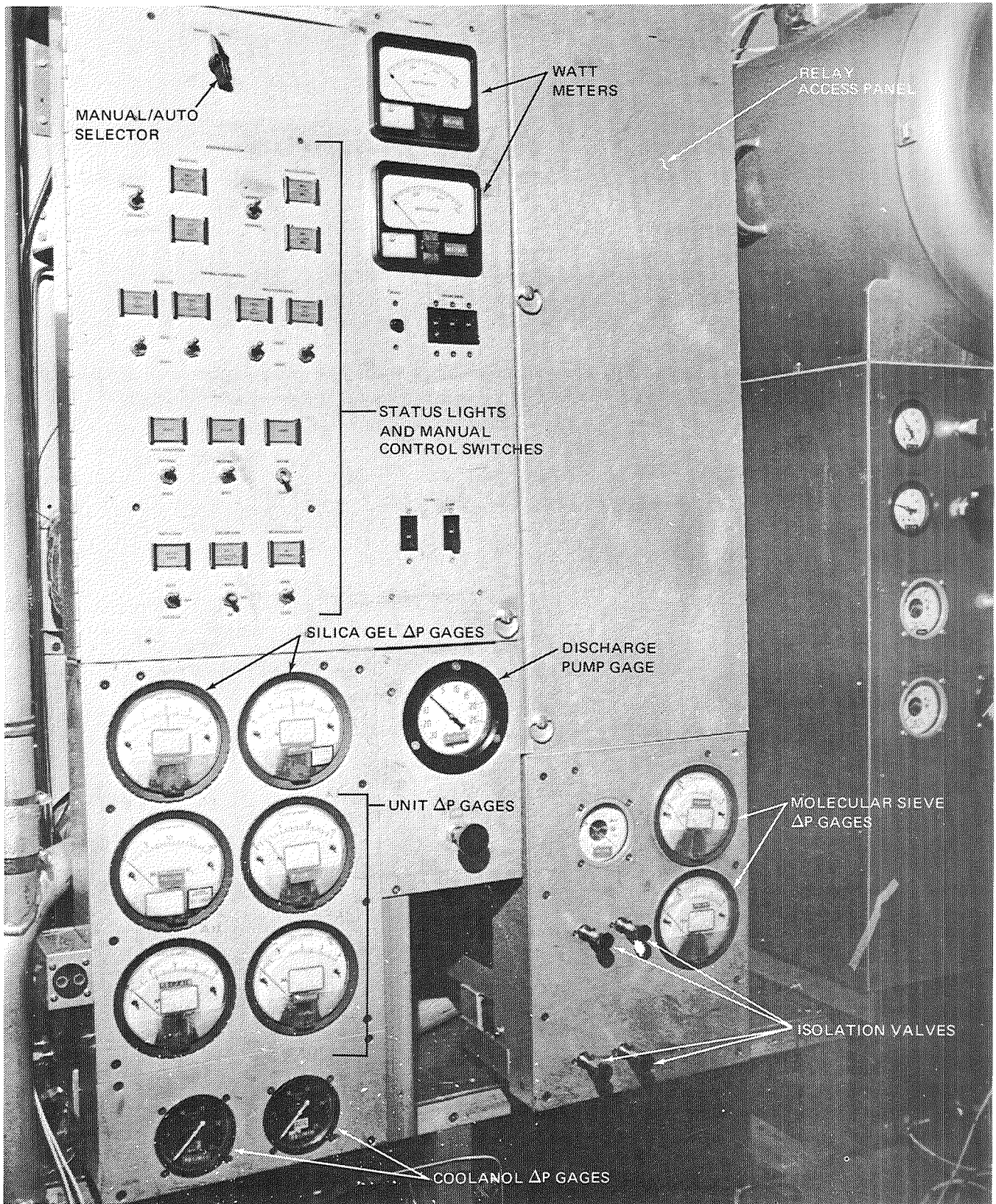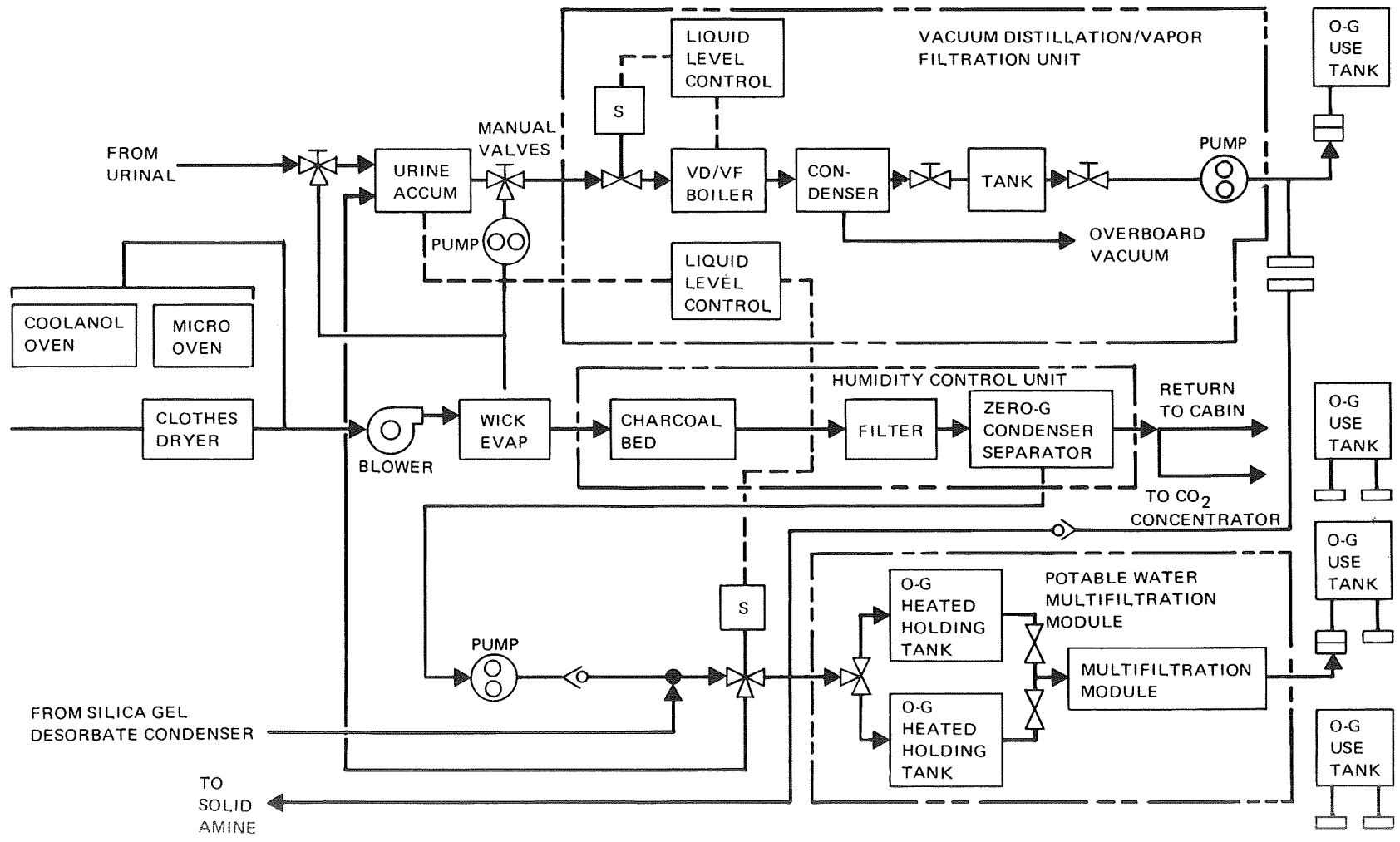
Figure 2. Molecular Sieve CO_2 Concentrator Unit

Figure 3. Integrated Potable Water and Humidity Control Subsystem Schematic
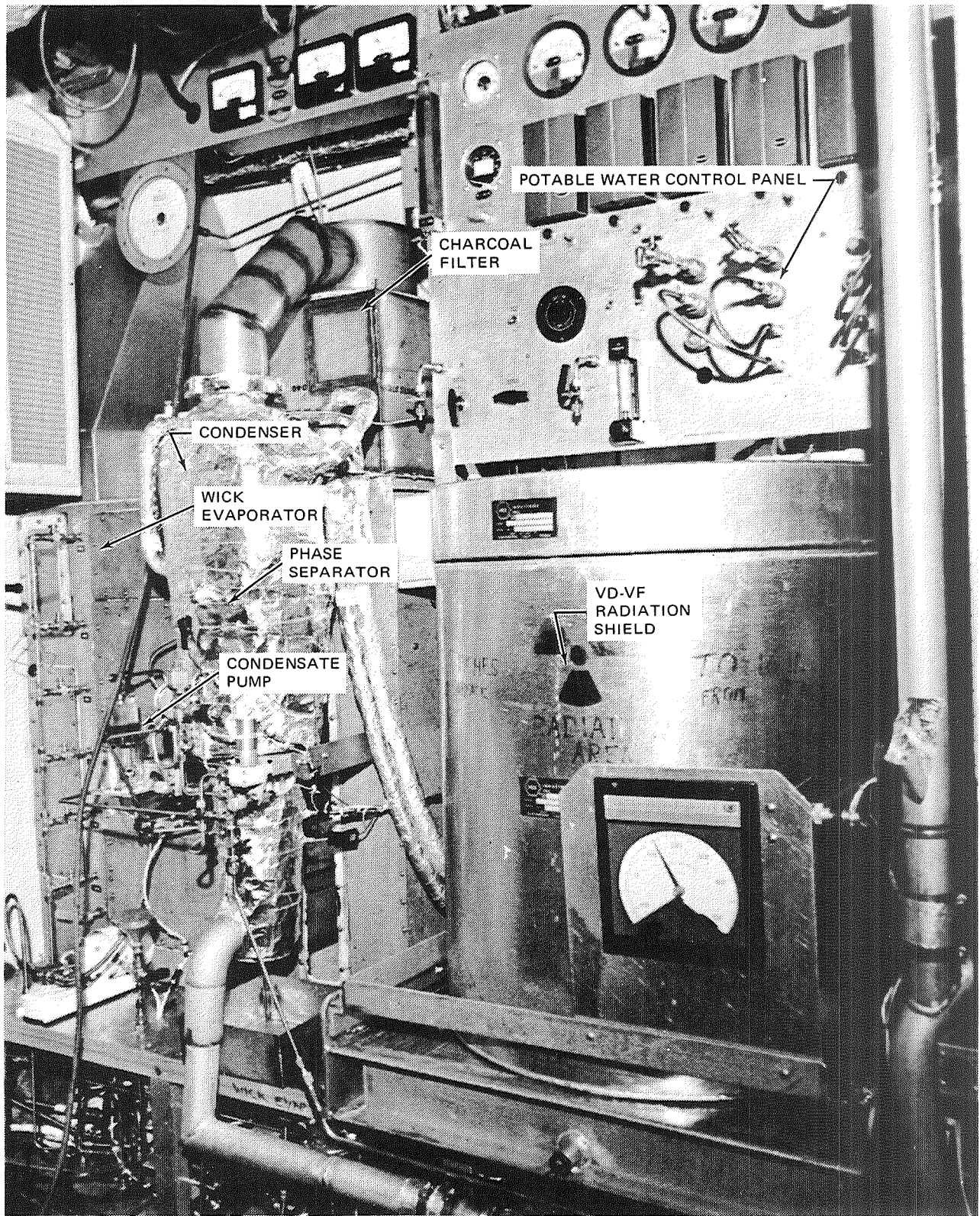
Figure 4. Potable Water Recovery Units—Humidity Control Unit, Air Evaporation Unit, VD-VF Unit, Water Control Panel

When the wick evaporator unit was used to recover potable water from urine, the pretreated urine was pumped to one of the wick packages. At this point the urine solids were deposited in the wick fibers and heated cabin air was used to vaporize the urine water. The vapors were then passed through an 11 kg (24 lb.) activated charcoal bed where most organic and inorganic contaminants were adsorbed. They were then passed through a condenser/separator. The condensed water was then pumped into the holding tanks in the detoxifications/multifiltration unit. The wick evaporator unit was used to process urine during 31 days while the humidity control portion of the unit operated for the entire 90-day test period. The 11 kg air carbon canister satisfactorily removed all urine odors and organic constituents from the gas stream during the entire 90 days. Samples from this charcoal material were taken at the end of the 90-day test to determine types and quantities of adsorbed compounds.

2.3 Hopcalite Catalyst

The Hopcalite catalyst analyzed in this program was removed from the toxin burner, which is a component of the Integrated Sabatier Reactor/Toxin Control Unit, after completion of the 90-day test. This unit is shown in Figures 5 and 6. Analyses were also performed on a white powder collected at the end of the discharge tube of the toxin burner and on the impingement area of the wall immediately behind the unit.

The basic components of the toxin burner are: a regenerative heat exchanger, an electric heating element, a temperature controller, and a catalytic (Hopcalite) reactor. The Hopcalite catalyst promotes the oxidation of carbon monoxide, hydrocarbons and methane to carbon dioxide and water vapor. This reaction occurs at a temperature of $588-643^{\circ}K$ ($315^{\circ}C$ - $370^{\circ}C$) in the presence of the Hopcalite catalyst. To maintain reaction conditions, heat must be added to the system.

HEATER

CATALYTIC BED

REGENERATIVE HEAT EXCHANGER

CABIN AIR

CABIN AIR

CO_2 FROM ACCUMULATOR

FILTER

ORIFICE

H_2 FROM ELECTROLYSIS UNIT

FILTER

ORIFICE

SABATIER REACTOR

O-G CONDENSER
O-G SEPARATOR

SPACE VACUUM EXHAUST

WATER TO ELECTROLYSIS UNIT

STORAGE TANK

CH_4

FILTER

ORIFICE

COOLING
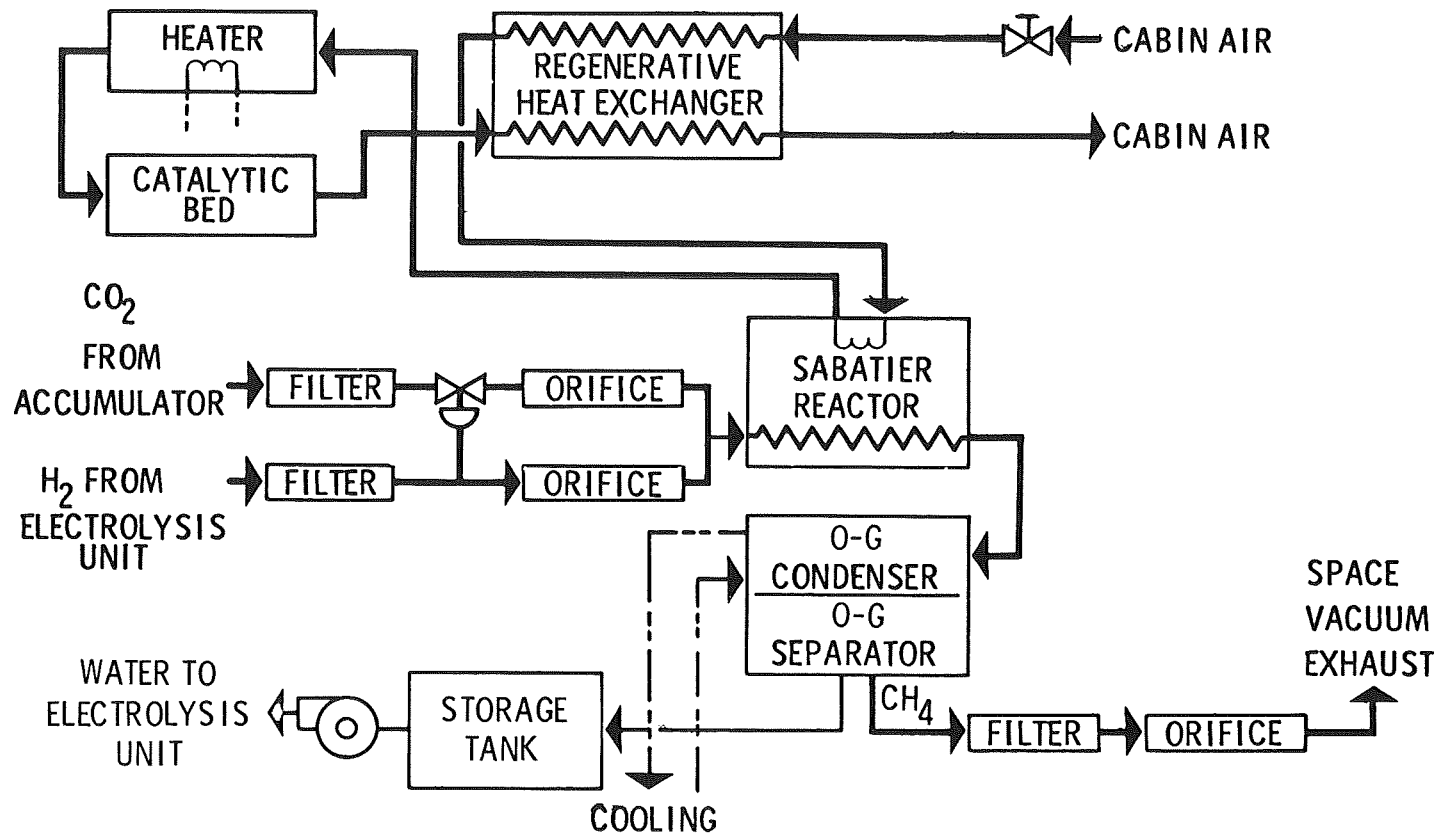
Figure 5. Integrated Sabatier and Toxin Control

WASTE MANAGEMENT
VACUUM CONTAINER

SABATIER/TOXIN
CONTROL UNIT
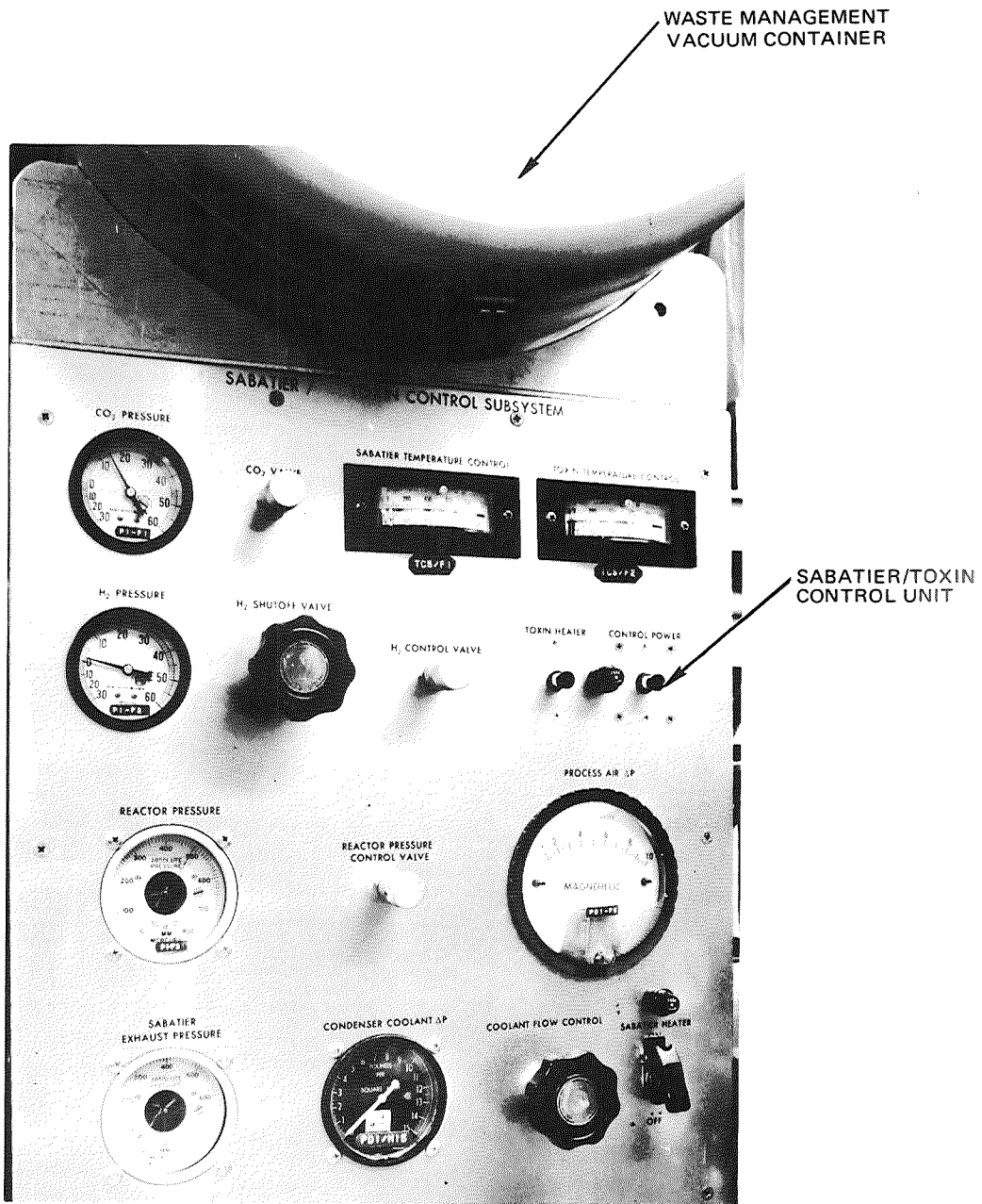
Figure 6. Sabatier Reactor/Toxin Control Unit - Control Panel

2.4 Nickel Catalyst

The nickel catalyst analyzed in this program was removed from the Sabatier reactor component of the Integrated Sabatier Reactor/Toxin Control Unit (Figures 5 and 6). The Sabatier reaction depends upon the catalytic activity of nickel on Kieselgur. When carbon dioxide from the CO_2 concentrator and hydrogen from water electrolysis react in the presence of the nickel catalyst, methane and water are formed. The water returns to the electrolysis unit while methane and other noncondensible exhaust gases are discarded overboard.

Section 3

TEST CONDITIONS AND PROCEDURES

3.1 Calibration of Gas Chromatographs

The materials desorbed from each of the three types of sorbents were first
identified by gas chromatography and then confirmed by mass spectrographic
analyses.

Two Perkin-Elmer gas chromatographs, Model 800, were used. Each instrument
was equipped with 12-foot dual columns and dual flame ionization detectors.
The columns of one instrument were packed with didecylphthalate (DDP) on
Chromosorb W, 80-100 mesh; the columns of the second instrument contained
Carbowax (CW) 1500 on Chromosorb W. Helium was the carrier gas in both
instruments. A flow rate of about 30 ml/min was maintained. Gas samples of
known composition were then introduced into each of the two gas chromatographs,
while the column temperature was maintained at 373°K (100°C). Thus, two elution
times were obtained, one with each instrument. Two additional elution times
were obtained for the same compound when the column temperatures were lowered
to 323°K (50°C).

A total of 75 organic compounds were calibrated. This list is shown on Table 1.
The compounds were selected on the basis of materials identified in the SSS
atmosphere by MDAC-W and other workers in this field. These calibrations were
repeatedly checked and brought up to date. They were then used to identify
unknown samples by matching the exhibited elution times with the tabulated data.
Whenever all four elution times from a sample matched all four elution times
of the calibrated material, the identification of the samples was assumed to be
positive. At times, preliminary identifications had to be based on three elution
peaks if the fourth one was covered by an interferring major peak from another
substance. In these instances, it was possible to confirm the identification by
mass spectrographic analyses.

Table 1

COMPOUNDS FOR WHICH CALIBRATION OF GAS
CHROMATOGRAPHS IS MAINTAINED

Compound	Compound
Ethyne (acetylene)	Propanol (Propyl alcohol)
Methane	Tetrahydrofuran
Propane	Cyclohexane
2-Methylpropane (isobutane)	Heptane
Ethanal (acetaldehyde)	2-Octene
2-Methylbutane (isopentane)	2-Butanol (sec-butyl alcohol)
Pentane	Tetrachloromethane (carbon tetrachloride)
2,2-Dimethylbutane	1,1,1-Trichloroethane (methyl chloroform)
Ethoxyethane (ethyl ether)	Trichloromethane (chloroform)
Furan	Benzene
2-Methyl-1,3-butadiene (isoprene)	2-Methyl-4-butanal (isovaleraldehyde)
Methanal (formaldehyde)	2-Methyl-1-propanol (isobutyl alcohol)
Propanal (propionaldehyde)	1,2-Dichloroethane (ethylene dichloride)
Methanol (methyl alcohol)	Propyl ethanoate (propyl acetate)
Ethyl methanoate (ethyl formate)	Methyl methacrylate
3-Methylpentane	3-Pentanone (diethyl ketone)
Propenal (acrolein)	2-Pentanone (methyl propyl ketone)
Ethanol (Ethyl alcohol)	Trichloroethylene
2-Propanone (acetone)	Pentanal (valeraldehyde)
Hexane	Dioxane
2-Propanol (Isopropyl alcohol)	Butanol (butyl alcohol)
1-Hexene	n-Octane
Carbon disulfide	4-Methyl-2-pentanone (methyl isobutyl ketone)
2-methyl-2-propanol (tert butyl alcohol)	1-Heptene
Dichloromethane (methylene chloride)	1-Toluene
2-Methylfuran	Ethanoic acid (acetic acid)
Ethyl ethanoate (ethyl acetate)	
Butanal (n-butyraldehyde)	
2-Propen-1-ol (Allyl alcohol)	
2-Butanone (methyl ethyl ketone)	

Table 1 (Continued)

Compound

Butyl ethanoate (butyl acetate)

3-Methyl-1-butanol (isoamyl alcohol)

1-Pentanol (amyl alcohol)

Ethyl benzene

1,4-Dimethylbenzene (p-xylene)

1,3-Dimethylbenzene (m-xylene)

1,2-Dimethylbenzene (o-xylene)

Pentyl ethanoate (pentyl acetate)

2-Ethoxyethanol acetate
(cellusolve acetate)

2-Ethyl-1-butanol

Isopropylbenzene (cumene)

Cyclohexanone

1,3,5-Trimethylbenzene
(mesitylene)

1,2,4-Trimethylbenzene
(pseudocumene)

Trichlorotrifluoroethane
(Freon 113)

2-Methyl-1-pentene

Ethane nitrile (acetonitrile)

2-Ethyl-1-hexanol

Methylethyl Acetate (isopropyl acetate)

3.2 Optimum Desorption Conditions

A procedure for the optimum desorption of contaminants from silica gel (SG), molecular sieve (MS) and activated charcoal (Act. C.) was established. The apparatus used for the desorption procedure is shown in Figure 7. A known amount of SG, MS and Act. C was placed into a 500-ml Erlenmeyer flask. By means of a heating mantle, the temperature of the material inside the flask was raised to $348°K$ ($75°C$), $398°K$ ($125°C$), $448°K$ ($175°C$) and $523°K$ ($250°C$) during successive test runs. During the heating process, the pressure inside the flask was maintained below 530 N/m^2 (4 mm Hg). The desorbed gases were carried by a very low helium flow to a brine trap $253°K$ ($-20°C$) where most of the water was condensed. The desorbed gases were then swept into a U-shaped stainless steel trap immersed in liquid nitrogen. Samples of 5 ml from this trap were then introduced into the two gas chromatographs and the peak heights obtained at the four different temperatures were compared.
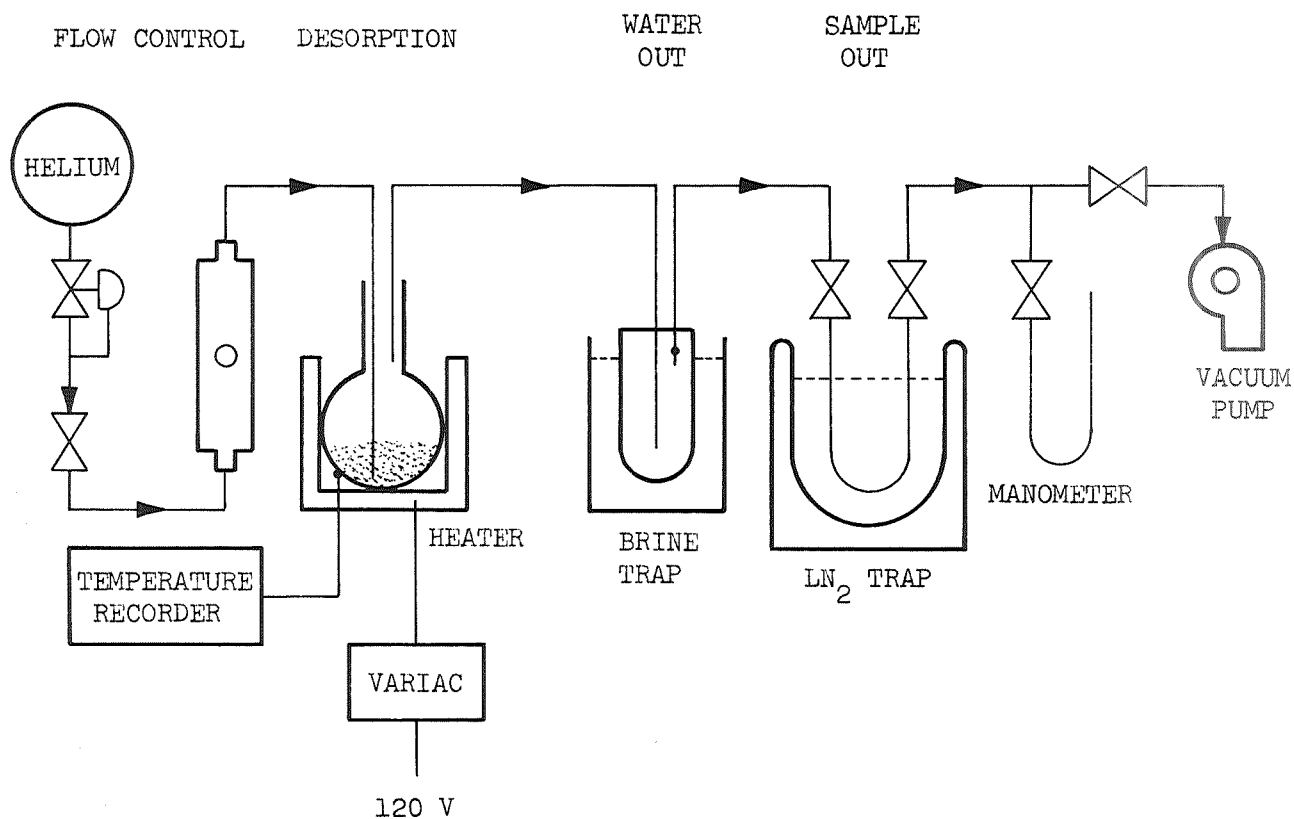
FIGURE 7. DESORPTION APPARATUS

Measurements were made of the quantities of organics, expressed in micrograms of toluene for each gram of sorbent. Toluene was selected because it was desorbed from each sorbent and exhibited a prominent peak in most chromatograms.

Table 2

Effect of Temperature on Quantities of Organics (Toluene) Recovered from Sorbents

(Sample Size: 1 gm Sorbent)

Desorption Temperature	Quantities of Organics (Toluene) Desorbed (μg/gm of sorbent)		
	Mol Sieve	Silica Gel	Activ. Charcoal
348°K (75°C)	0.00737	0.00553	8.470
398°K (125°C)	0.01659	0.01660	39.770
448°K (175°C)	0.03501	0.03413	152.361
523°K (250°C)	0.01474	0.02029	162.691

Results in Table 2 indicate that a desorption temperature of 448°K (175°C) was close to optimum, since the largest quantities of organic materials were found to desorb in this range.

To determine the optimum sampling time, one sample of each sorbent was desorbed in successive 40-minute time intervals. The amount of toluene eluted during each sampling period was determined. Table 3 shows the results of these successive desorptions.

Table 3

Effect of Sampling Time on Quantities of Organics (as Toluene)

Desorbed From 3 Sorbents

Sample Size: 1 gram

Quantities of Organics (Toluene) Desorbed

(micrograms per gm of sorbent)

Sampling Time	Mol Sieve	%	Silica Gel	%	Activ. Charcoal	%
First 40 min.	.1108	61.23	.0351	86.38	264.700	88.75
Second 40 min.	.0166	9.19	.0018	4.54	22.597	7.57
Third 40 min.	.0249	13.77	.0009	2.27	4.906	1.64
Fourth 40 min.	.0120	6.64	.0009	2.27	4.132	1.39
Fifth 40 min.	.0092	5.11	.0018	4.54	1.090	0.37
Sixth 40 min.	.0074	4.08	--	--	0.026	0.28

The results of this test indicate that silica gel and activated charcoal release 86.38% and 88.75% of adsorbed organics during the first 40-minute desorbing period, if the desorption temperature is maintained at $448^{\circ}K$ ($175^{\circ}C$); the desorption of molecular sieve under identical conditions is 61.23%. Based on the data in Tables 2 and 3, further desorptions were done at a desorbing temperature of $448^{\circ}K$ ($175^{\circ}C$) and a desorbing time of 40 minutes.

Section 4

TEST RESULTS

4.1 Molecular Sieve, Silica Gel and Activated Charcoal Analysis

During the 90-day run two silica gel beds were used. When the unit was shut
down, silica gel #1 bed was near the end of the desorbing cycle, while
silica gel #2 was near the end of the adsorbing cycle as shown in Figure 8.
Each of the beds contained approximately 3.8 kg (8.3 lbs) of silica gel. To
obtain representative samples, each bed of silica gel was divided into a top,
a center, and a bottom portion, each containing about one third of the total
silica gel used. It was noted that the top portion had a number of yellow-brown
crystals, the center portion was colorless, while the bottom portion was light
yellow. The three portions of the silica gel were analyzed separately.

The samples of molecular sieve beds #1 and #2 corresponded to the adsorption
and desorption cycles of the silica gel samples.   Each of the two beds contained
about 5.4 kg (11.8 lbs) of molecular sieve, as **weighed** at the end of the 90-day
test. Molecular sieve beds were also divided into top, center, and bottom
portions, each consisting of one third of the total molecular sieve sorbent
used. No visual differences between the three portions were found. The three
molecular sieve portions were also separately analyzed.

Activated charcoal samples were taken from the air evaporator bed which contained
11 kg (24 lbs) of this sorbent. Samples of charcoal were taken near the top
of the bed and from the center and bottom. The portions were combined to form
one homogenous sample. Unused charcoal from the same manufacturer was used for
baseline determinations. The amounts of organic compounds observed in the base-
line chromatograms were negligible compared with the large quantities of organics
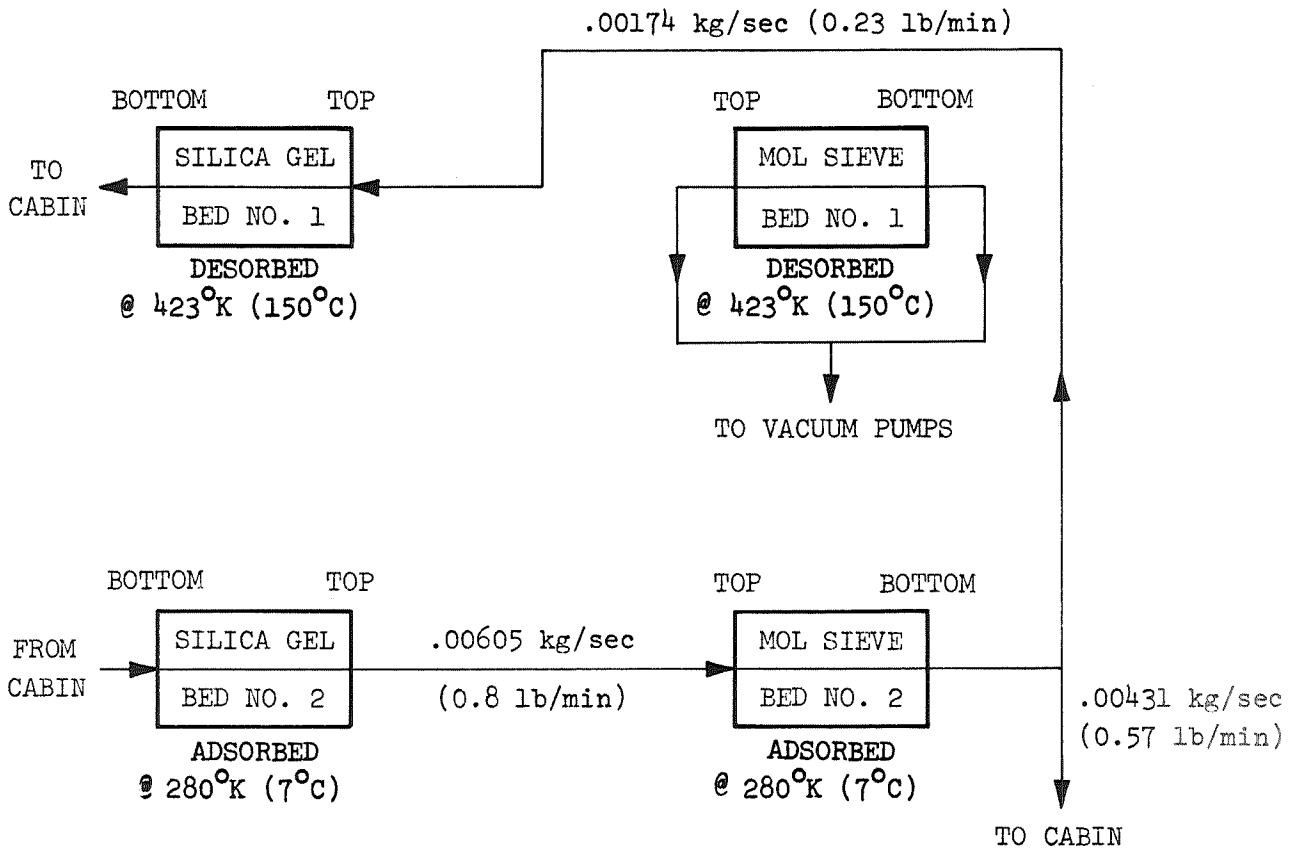desorbed from the used charcoal.

FIGURE 8 CO_2 CONCENTRATOR FLOW AT CONCLUSION OF 90-DAY TEST

4.1.1 Organic Compounds

The desorption of organic materials from the three sorbents was carried out according to the procedures derived in Section 3. Assignment of individual chromatographic peaks to specific compounds was based on calibrated elution times, as previously described. Agreement of four elution times with the calibrated values was considered sufficient for positive identification. In most instances mass spectrographic analyses provided final confirmation of gas chromatographic identification.

The types and quantities of organic compounds driven off the three sorbents are shown in Tables 4, 5 and 6. The number of organic compounds released by the three sorbents varied from 12 for silica gel to 14 for molecular sieve and activated charcoal. This compares to approximately 40 compounds identified during the 60-day run (Reference 1).

The mass spectral analyses of desorbate from the activated charcoal revealed the presence of trifluoromethane. This compound is in all likelihood derived from the use of Freon 113, the only fluorine containing solvent introduced into the SSS. The identification of a fluorinated compound is important since in all previous tests only chlorine containing compounds were identified. Concentrations desorbed from silica gel and molecular sieve sorbents were generally too low to obtain a sufficient sample size of this highly volatile material for detection by gas chromatography and mass spectrometry.

The presence of ethanenitrile (acetonitrile) originally identified by NASA-LaRC by microwave spectroscopy during the 60-day run was also confirmed in the 90-day test. This compound was identified in the desorbates of silica gel and charcoal.

4.1.1.1 Quantitative Determination of Desorbed Compounds

After identification of gas chromatographic peaks and confirmation by mass spectroscopy, it was important to determine concentration levels of individual contaminants driven off the sorbents. This involved quantitative calibration of one gas chromatograph with the organic compounds of interest. Known quantities of specific materials were introduced into the 5-ml sample loop of

Table 4   Desorbates From Silica Gel (in μg/g sorbent)

	Top		Center		Bottom	
	Silica Gel-1	Silica Gel-2	Silica Gel-1	Silica Gel-2	Silica Gel-1	Silica Gel-2
Total Volume	27 mℓ	27 mℓ	27 mℓ	27 mℓ	27 mℓ	27 mℓ
1. Trichlorotrifluoroethane (Freon 113)	69.000	15.000	2.300	9.656	37.170	10.100
2. Propanone (Acetone)	--	--	.1662	.896	6.120	1.224
3. Ethane nitrile (Acetonitrile)	.793	.631	--	--	--	--
4. Benzene	.0199	--	.0567	.00795	.0179	.0119
5. 1,2-Dichloroethane	.289	.0633	.0768	.3706	.5966	.2441
6. Octane	.188	--	.00672	.0235	.0403	.1142
7. Butanol (Butyl alcohol)	3.474	--	.0161	--	.0804	--
8. 1,4-Dimethylbenzene (p-xylene)	.129	.0309	.00845	--	--	--
9. 2-Ethyl-1-butanol	.100	.00773	.0116	--	.0387	.0271
10. Dichloromethane (Methylene chloride)	4.983	.671	--	--	--	--
11. 4-Methyl-2-pentanone (Methyl isobutyl ketone)	--	.0805	--	--	--	--
12. Toluene	.0565	.153	.00706	--	--	--

Table 5 Mol Sieve Desorbates in µg/g of Sorbent (DDP-50)

	Top		Center		Bottom	
	MS-1	MS-2	MS-1	MS-2	MS-1	MS-2
Total Volume	27 ml	127 ml	27 ml	114 ml	27 ml	47 ml
1. Trichlorotrifluoroethane (Freon 113)	.106	1.588	--	1.206	.0434	.0514
2. Propanone (Acetone)	.00656	--	.00659	--	.00328	--
3. Dichloromethane (Methylene chloride)	.0719	--	.0623	.202	.0527	--
4. Butanol (Butyl alcohol)	.0804	.0605	.0482	.339	--	.0559
5. 4-Methyl-2-Pentanone (Methyl isobutyl ketone)	.0137	--	--	--	--	.0149
6. Toluene	.0517	.1416	.0117	--	.00474	.00819
7. Pentane	.3536	--	.6151	1.1362	.2760	.2190
8. Hexane	.0463	--	--	--	.00198	.00346
9. 1,2-Dimethylbenzene (o-xylene)	.0789	--	--	--	--	--
10. Tetrachloromethane (Carbon Tetrachloride)	--	--	.0128	--	.00766	.00444
11. 1,2-Dichloroethane	--	--	.1220	--	.0588	--
12. 1-Heptene	--	--	--	--	.00206	.001194
13. 2-Ethyl-1-butanol	--	--	.0155	.01958	--	.03364
14. Octane	--	--	--	--	.03022	--

TABLE 6 ACTIVATED CHARCOAL DESORBATES

Air Evap, DDP-50°C

Identified Organic Compounds	µg/g sorbent
1. 2-Methylpropane (Isobutane)	8.546
2. 3-Methylbutane (Isopentane)	16.637
3. Pentane	11.740
4. Trichlorotrifluoroethane (Freon 113)	3035.000
5. 2-Propanone (Acetone)	21.400
6. Hexane	24.977
7. Ethanenitrile (Acetonitrile)	2.703
8. 2-Butanone (Methyl ethyl ketone)	44.829
9. Tetrachloromethane (Carbon Tetrachloride)	46.489
10. Benzene	16.699
11. 1,2-Dichloroethane	63.275
12. Butanol (Butyl alcohol)	36.024
13. Toluene	263.417
14. 2-Ethyl-1-butanol	51.949
15. Trifluoromethane*	

* Not quantitated.

the gas chromatograph and the peak heights produced with different concentrations were determined. This provided a measure of the concentration of the specific compounds in terms of parts per million by volume, or in weight of the specific compound released per gram of sorbent. All calibrations of the 17 organic compounds shown in Table 7 were carried out with didecyl phthalate columns at a temperature of $323°K$ ($50°C$). The Table shows the peak heights, in recorder divisions, produced by each of 17 organic compounds, based on 1 ppm of each compound. Total organics were later estimated by using average values of peak height and molecular weights.

4.1.1.2 Identification and Analysis of Desorbates

The first columns of Tables 4 and 5 show the individual organic compounds identified. The volume of desorbate which was collected in the stainless steel traps immersed in liquid nitrogen varied from 27 ml to 127 ml when returned to atmospheric pressure and temperature. The samples which were analyzed were taken from the top, center, or bottom parts of the silica gel and molecular sieve sorbents. The desorbing cycle is expressed by Silica Gel-1 or Mol Sieve-1, while the adsorbing cycle reads Silica Gel-2 or Mol Sieve-2.

The desorbates from activated charcoal used in the air evaporator during the entire 90-day run are shown in Table 6. In this case three charcoal samples were taken from three locations of the charcoal bed. They were then combined into one single sample representative of the entire bed.

The quantitative analytical results are expressed in micrograms of contaminant per gram of sorbent. It will be noted that the amounts of organics desorbed from the silica gel sorbent are considerably higher than from molecular sieve. This could be due to the fact that during the 90-day run silica gel desorption took place at the ambient cabin pressure, while the molecular sieve was desorbed at about 13.4 kN/m^2 (100 mm Hg). Both types of beds were desorbed at approximately $423°K$ ($150°C$).

TABLE 7 - QUANTITATIVE CALIBRATIONS

		Recorder Divisions per ppm	Molecular Weight
1.	Propanone (Acetone)	21.7	58.1
2.	Toluene	16.0	92.1
3.	Tetrachloromethane (Carbon Tetrachloride)	2.46	153.8
4.	2-Butanone (Methyl ethyl ketone)	16.1	72.1
5.	Trichlorotrifluoroethane (Freon 113)	31.3	187.4
6.	Trichloroethylene	7.16	131.4
7.	Benzene	32.1	78.1
8.	1,2-Dichloroethane	8.95	99.0
9.	Butanol (Butyl alcohol)	1.88	74.1
10.	Ethanenitrile (Acetonitrile)	3.7	41.1
11.	4-Methyl-2-Pentanone (Methyl isobutyl ketone)	23.9	100.2
12.	Octane	13.9	114.2
13.	Hexane	53.3	86.2
14.	Dichloromethane (Methylene Chloride)	7.24	84.9
15.	Pentane	84.4	72.2
16.	Heptene-1	58.5	98.2
17.	2-Methylpropane (Isobutane)	105.0	58.1

The quantities of 2-ethyl 1-butanol, a decomposition product of Coolanol-35, were lower than those observed in the previous 60- and 30-day tests. By using better leak check procedures and improved valves and fittings, a system with a minimum of Coolanol leaks was obtained which resulted in much lower concentrations of this compound in the atmosphere.

The highest amounts of organic compounds were driven off the activated charcoal bed. This sorbent had been in continuous use for the entire 90-day run. It may also be of interest that the quantities of organic compounds desorbed from top and bottom silica gel samples are considerably higher than the organics released by the center portion of the bed. It was mentioned before that each portion of the silica gel had a different color. However, it is at this time not certain whether this difference in color was in any way related to the types and quantities of released contaminants.

Not only the number of identified contaminants were lower than in previous runs, their concentrations were also considerably lower. Sole exceptions were the Freon 113 and certain related halogenated compounds. The generally low number and low concentrations of contaminants observed indicates that the air inside the SSS was of exceptionally high purity.

4.1.2 Inorganic Compounds from Desorbates

The desorbed gases from the silica gel, molecular sieve and activated charcoal sorbents were also tested by wet chemical procedures for the presence of ammonia, oxides of nitrogen and sulfur dioxide. Neither silica gel nor molecular sieve sorbents showed the presence of any of the three contaminants. However, activated charcoal contained 170 µg of ammonia and 18.1 µg of oxides of nitrogen per gram of charcoal.

4.2 Hopcalite and Nickel Catalysts

The operation of the toxin burner and the Sabatier reactor are based on the efficiency of the Hopcalite and nickel catalysts respectively. Malfunctioning of the nickel catalyst resulted in the inability to sustain a reaction in the bed. This reaction is normally exothermic and self sustaining as long as

reactants are supplied, but failed with increasing frequency during the first 29 days of the 90-day test.

Data from the 90-day test (Reference 2) shows that the Hopcalite catalyst was active throughout the period. Quantitative measurements of capacity were not available, however, The possibility exists that some damage to the Hopcalite and the complete loss of activity of the nickel catalysts were caused by their adsorption of the halogens from Freon 113. Samples of the two catalysts which had been used during the 90-day tests were analyzed together with unused materials which served as "blanks."

4.2.1 Hopcalite

Analysis of compounds desorbed from Hopcalite showed the presence of chlorides at a concentration of 0.3 mg per gram of Hopcalite, and of ammonia at a concentration of 0.056 mg per gram of Hopcalite. No oxides of nitrogen, sulfur dioxide, or other inorganic or organic compounds were detected. The unused Hopcalite "blanks" were free of chlorides, ammonia, and organic compounds.

A white powder at the outlet of the toxin burner was collected at the end of the test. Qualitative analysis of this powder showed a high concentration of chlorides. The presence of fluoride was not specifically identified because it was obscured by the high chloride content. Analysis of the powder by atomic adsorption spectroscopy showed the following major constituents; iron, aluminum, nickel, and copper, besides several minor trace constituents. These major metallic constituents may have originated in the Hopcalite catalyst or from attack of the tubing or heat exchanger downstream of the catalyst bed by the highly corrosive decomposition products of the Freon.

4.2.2 Nickel on Kieselgur

A literature survey indicated that metallic nickel and, to a smaller extent, metallic oxide catalysts may be adversely affected or completely destroyed by compounds containing halogen and sulfur groups (Reference 4). Since Freon 113 contains both chlorine and fluorine, the possibility exists that the thermal decomposition of this solvent under reactor conditions contributes to the deterioration of the catalyst. The ensuing halogenated materials will also adversely

affect the stainless steel and aluminum components of the unit.

In view of the catalyst poisoning experience, it was important to know the composition of the gas stream reaching the Sabatier catalyst. As reported in Reference 2, analyses of the gas stream from the CO_2 concentrator showed the presence of Freon 113 at a concentration of 5.0 to 39.0 ppm, with a median of 11.2 ppm, in addition to small amounts of ethanol and propanone (acetone).

On the 29th day of the 90-day test, the spent nickel catalyst was replaced with new material. The latter was protected by placing an activated carbon filter in the CO_2 line. Analysis of gas samples taken downstream of the carbon filter showed that the Freon 113 was initially almost completely removed.

Three samples of nickel catalyst of different origins were analyzed for chloride ions and for organic compounds.
Sample A consisted of spent nickel catalyst used during the first 29 days of the 90-day run.
Sample B was the catalyst used during the remainder of the 90-day run.
Sample C was unused nickel catalyst which served as "blank."

The amounts of chloride ions found in Samples A, B, and C were:
Sample A - 6.24 mg chloride ions/gm of Ni catalyst
Sample B - 1.92 mg chloride ions/gm of Ni catalyst
Sample C - 0.96 mg chloride ions/gm of Ni catalyst

Deducting the "blank" concentration found in the unused nickel catalyst from the values of Samples A and B, the net values obtained were 5.28 mg chloride and 0.98 mg chloride respectively, per gram of nickel catalyst.

The amounts of total organic compounds found in Samples A, B, and C were:
Sample A - 0.569 µg organics/gm Ni catalyst
Sample B - 0.048 µg organics/gm Ni catalyst
Sample C - None

The organic compounds desorbed from the catalyst were propanone, 3-methylpentane, hexane, 1,1,1-trichloroethane, 3-pentanone, and toluene.

Although an activated charcoal trap was placed in the CO_2 line to remove halogenated and organic compounds, a small amount reached the nickel catalyst since the trap was bypassed for a short period whenever the charcoal was replaced. The charcoal was replaced five times during the last 60 days of the test (Reference 2).

A metal analysis of the nickel catalyst by atomic adsorption showed nickel and silicon as major components. Present in trace amounts were boron, phosphorus, manganese, iron, magnesium and lead. These elements were normally present in the nickel catalyst. The unused sample was completely free of contaminants.

CONCLUSIONS

1. Qualitative analyses of desorbates from three sorbent beds, silica
   gel, molecular sieve, and activated charcoal led to the identification
   level of 12 to 14 organic contaminants. This compares to approximately
   40 compounds identified in the 60-day run.

2. In addition to the smaller number of identified compounds, their
   quantities were also significantly lower than in previous runs.

   Low number and low concentrations of contaminants observed during
   the entire 90-day run indicated that the air inside the SSS was of
   very high purity.

3. Amounts of organic compounds desorbed from silica gel sorbent were
   considerably higher than from molecular sieve. The highest amounts
   of organic compounds were driven off the activated charcoal bed.
   This sorbent had been in continuous use for the entire 90-day run.

4. Neither silica gel nor molecular sieve sorbents showed the presence
   of ammonia, oxides of nitrogen or sulfur dioxide. Activated charcoal
   was found to desorb ammonia and oxides of nitrogen but no sulfur
   dioxide.

5. Hopcalite and Nickel catalysts may be gradually deactivated or
   completely destroyed by interaction with halogenated hydrocarbons.
   These compounds may be formed by thermal decomposition of Freon 113.

6. Performance of the nickel catalyst in the Sabatier reactor was lost
   during the first 29 days of the 90-day test. Analysis of this catalyst
   indicated the presence of quantities of halogen impurities. Reactor
   performance was restored by replacing the catalyst.

7. By placing an activated charcoal bed ahead of the nickel catalyst of the Sabatier reactor the Freon 113 contaminants were effectively trapped, thereby preventing the **formation of chlorinated compounds** and degradation of the catalyst.

8. No quantitative evidence indicates that deterioration of the Hopcalite catalyst had occurred. However, halogen impurities were detected in the catalyst bed after test completion, and in the exhaust tubing of the unit.

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